

Water Dramatically Accelerates the Decomposition of α -Hydroxyalkyl-Hydroperoxides in Aerosol Particles

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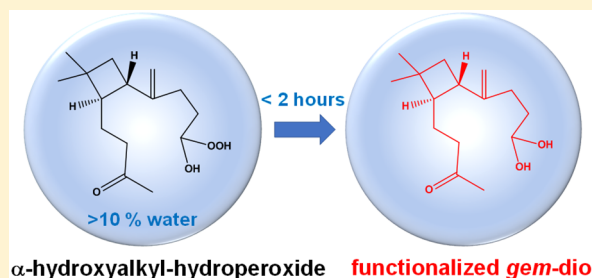
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Supporting Information

ABSTRACT: α -Hydroxyalkyl-hydroperoxides (α -HHs), from the addition of water to Criegee intermediates in the ozonolysis of olefins, are reactive components of organic aerosols. Assessing the fate of α -HHs in such media requires information on the rates and products of their reactions in aqueous organic matrixes. This information, however, is unavailable due to the lack of analytical techniques for the detection and identification of labile α -HHs. Here, we report the mass spectrometric detection (as Cl^- adducts) of the α -HH produced in the ozonolysis of a C_{15} diolefin in water (W):acetonitrile (AN) mixtures of variable composition containing inert NaCl. α -HH decays into a *gem*-diol + H_2O_2 within $\tau_{1/e} \approx 52$ min in 50% (v:v) water, but persists longer than a day in $\leq 10\%$ water mixtures. The strong nonlinear dependence of $\tau_{1/e}$ on solvent composition reveals that water content is a major factor controlling the fate of α -HHs in atmospheric particles. It also suggests that α -HH decomposes while embedded in W_nAN_m clusters rather than randomly dissolved in molecularly homogeneous W:AN mixtures.



In tropospheric organic aerosols, α -hydroxyalkyl-hydroperoxides (α -HHs) are produced from the ozonolysis of olefins in the presence of water. The mechanism of α -HH formation begins with the electrophilic addition of O_3 to $\text{C}=\text{C}$ double bonds into primary ozonides,¹ which rapidly decompose into carbonyl oxide zwitterions/diradicals known as Criegee intermediates (CIs).^{2–4} CIs can fragment, isomerize, or add hydroxylic species, such as water, alcohols, and carboxylic acids.^{5–7} CIs reactions with water produce the bifunctional α -HHs: $\text{R}(\text{H})\text{C}(\text{OH})\text{OOH}$.⁸ α -HHs are thermally unstable species that have proved to be difficult to isolate and analyze.^{9,10}

The ozonolysis of the massive biogenic olefin (isoprene and mono- and sesquiterpenes) emissions is a global source of α -HHs in the troposphere.^{11–14} Current interest in the atmospheric chemistry of α -HHs owes to the fact that their $-\text{OOH}$ functionalities are deemed to be involved in aerosol aging.^{15–18} α -HHs, due to the presence of both $-\text{OH}$ and $-\text{OOH}$ polar groups, have relatively low vapor pressures and partition to condensed environmental phases, such as fog, aqueous aerosol droplets, and wet films.^{19–21} Most theoretical and experimental work, however, has focused on the decomposition of α -HHs in the gas phase,^{22–32} rather than in the more relevant aqueous organic phases.³³ Experimental studies in condensed phases have been hampered by the lack of analytical techniques for the fast, unambiguous identification of α -HHs and their decomposition products.^{8,20,34}

Recently, we reported that the neutral α -HHs produced from the hydration of mono- and sesquiterpene CIs can be detected by mass spectrometry as Cl^- adducts in the presence of inert NaCl.^{3,5–7,35} The same approach allowed the detection of the ester and ether hydroperoxides generated from CI reactions with carboxylic acids, alcohols, and saccharides.^{3,5–7,36} We consider that this novel approach for detecting neutral, labile organic α -HHs in the liquid phase without manipulation represents an optimal solution to a hitherto challenging task.^{34,37–40} Here, we apply this approach (Figure S1) to investigate the thermal decomposition of the α -HH generated in the ozonolysis of the sesquiterpene β -caryophyllene (β -C, $\text{C}_{15}\text{H}_{24}$, MW 204.35, a biogenic gas globally emitted to the troposphere) dissolved in water (W):acetonitrile (AN) mixtures of variable composition, reaction R1.



To our knowledge, this is the first report of rate constants for the decomposition of α -HHs, k_1 , as a function of water content in aqueous organic media. Experiments using D_2O and H_2^{18}O confirm that the decomposition of α -HH involves a

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water molecule and show that the organic product of reaction R1 is the *gem*-diol of a functionalized aldehyde.

Product Identification. Figure 1 shows negative ion mass spectra obtained (see the Experimental Section) from (1 mM

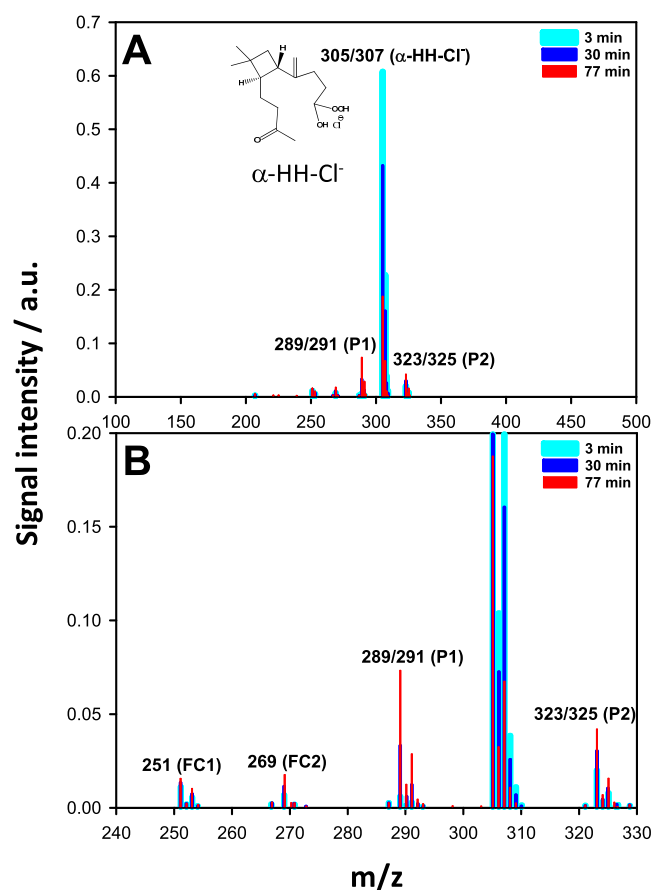


Figure 1. (A) Negative ion mass spectra of (1 mM β -caryophyllene + 0.2 mM NaCl + $[\text{O}_3]_0 = 0.04$ mM) in W:AN (50:50 = vol:vol; $[\text{H}_2\text{O}] = 27.8$ M) mixtures as a function of time. m/z 305/307 signals correspond to the chloride adduct of the α -HH (a representative structure of α -HH- Cl^- adducts among possible isomers shown in the inset). (B) Zooming-in on products in the $m/z = 240$ – 330 mass range.

β -C + 0.2 mM NaCl + $[\text{O}_3]_0 = 0.04$ mM) solutions in W:AN (50:50 = vol:vol, $[\text{H}_2\text{O}] = 27.8$ M) mixtures as a function of time.

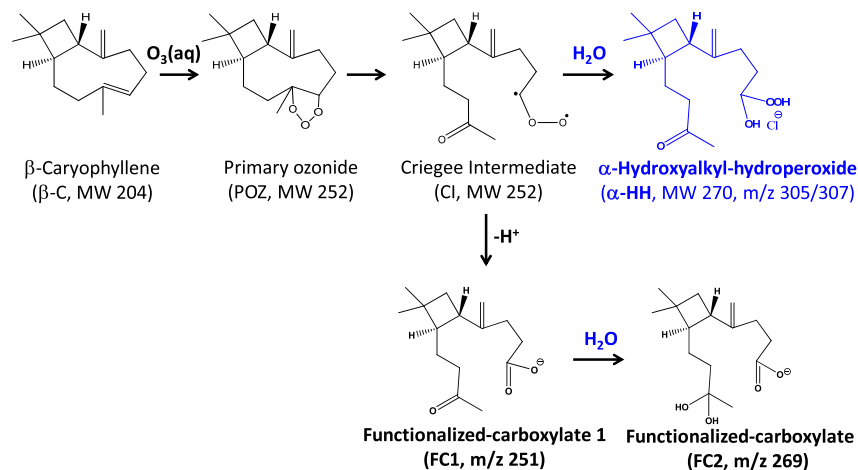
Upon mixing the 0.08 mM O_3 and 2 mM β -C + 0.4 mM NaCl solutions, O_3 is rapidly consumed by the β -C excess: $[\beta\text{-C}]_0/[\text{O}_3]_0 = 25$. From the reported gas-phase rate constant, $k(\beta\text{-C} + \text{O}_3)_{\text{gas}} \approx 1.1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,⁴¹ which translates into a liquid-phase rate constant, $k(\beta\text{-C} + \text{O}_3)_{\text{liquid}} \approx 6.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$,⁴² we estimate an O_3 half-life of 0.15 ms under present conditions, which is much shorter than the time scale of our experiments. On the basis of previous studies,⁴³ O_3 is deemed to mainly add to the endo double bond of β -C (see Scheme 1), producing a primary ozonide³ that opens up into a stabilized CI. However, we have evidence that a second O_3 molecule may also add to the β -C exo double bond during the mixing of solutions (see below). The CI isomerizes into a functionalized carboxylic acid (FC1, detected as a carboxylate) or adds water to produce an α -HH (Scheme 1).

The intense peaks at m/z 305/307 are therefore ascribed to the chloride adducts of α -HH, $305/307 = 204$ (β -C) + 48 (O_3) + 18 (H_2O) + 35/37 (Cl^-), in line with our previous observations.³ The incorporation of chloride is confirmed by the 3-to-1 ratio of 305/307 signal intensities, which corresponds to the ratio of natural abundance $^{35}\text{Cl}/^{37}\text{Cl}$ chlorine isotopes. We also detect species at m/z 251 (FC1), 269 (FC2), 289/291 (P1), and 323/325 (P2).

The time evolution of the various signals is consistent with the mechanism of Scheme 1. While the α -HH m/z 305/307 signals decay exponentially with time, as expected from the decomposition of a species produced at shorter times, the carboxylate FC1 signals remain constant, as expected from the stable products of a fast CI isomerization. The m/z 269 (FC2), 289/291 (P1), and 323/325 (P2) signals, in contrast, increase with time, albeit at different rates. The increasing m/z 269 (FC2) signals are consistent with the relatively slow hydration of the FC1 $\text{C}=\text{O}$ group. It should be realized that the different response factors of the various species (whose determination would require commercially unavailable samples) preclude establishing mass balances from measured mass signal intensities.

The m/z 323/325 (P2) signals detected at the beginning of the experiments deserve comment. Formally, the species

Scheme 1. Mechanism of β -Caryophyllene Ozonolysis in Aqueous Phases^a



^aWe show the most likely, among many, structural and stereo isomers (see text).

associated with the m/z 323/325 signals could be produced from H_2O (+18 Da) addition to the m/z 305/307 α -HH. Isotope labeling experiments, however, discriminate against this possibility (see the Experiments in D_2O :AN and H_2^{18}O :AN Solvent Mixtures discussion). They point to a species produced from O_3 additions to both the exo and endo double bonds of β -C, followed by the slow release of formaldehyde (H_2CO ; 30 Da) from the exo ozonide: $323/325 = 305/307 + 48 (\text{O}_3) - 30 (\text{H}_2\text{CO})$. This finding is consistent with theoretical calculations on the gas-phase ozonolysis of β -C, which predict that ozone also reacts with the exo double bond but to a smaller extent.⁴⁴ The evolution of m/z 323/325 signals in our experiments support this mechanism (see the Kinetic Measurements discussion).

We verified that the addition of 100 mM tetrahydrofuran (THF) (an efficient OH radical scavenger, $k_{\text{OH}+\text{THF}} = 2.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$)⁴⁵ to reaction mixtures has negligible if any effects; the same product signals appear at m/z 251, 269, 289/291, 305/307, and 323/325 (Figure S2). This finding excludes the participation of OH radicals in this system. We verified that the pH of the reacting solution remains at ~ 5.6 throughout (Figure S3).

Experiments in D_2O :AN and H_2^{18}O :AN Solvent Mixtures. The mass-specific characterization of the products formed in D_2O :AN and H_2^{18}O :AN solutions confirms the identity of products and the mechanism of α -HH decomposition. Figure 2 shows negative ion mass spectra obtained from (1 mM β -C + 0.2 mM NaCl + $[\text{O}_3]_0 = 0.04 \text{ mM}$) in D_2O :AN (50% by vol) and H_2^{18}O :AN (50% by vol) solutions.

The +2 mass units shift of the $m/z = 305/307$ signals to m/z 307/309 in both D_2O :AN and H_2^{18}O :AN confirms the involvement of a water molecule in the formation of α -HH (Scheme 1).³ The findings that (1) $m/z = 251$ signals do not shift whereas m/z 269 signals shift to m/z 270 (rather than to 271 as expected from the presence of two OH exchangeable groups in the gem-diol of FC2, due to residual H_2O in our setup) in D_2O :AN and (2) both signals shift by +2 Da to m/z 253 and 271 in H_2^{18}O :AN are consistent with the presence of a C=O group that rapidly exchanges O atoms with H_2^{18}O via reversible water addition: $-\text{C}(=\text{O}) + \text{H}_2^{18}\text{O} \rightleftharpoons -\text{C}(-^{16}\text{OH})(-^{18}\text{OH}) \rightleftharpoons -\text{C}(=\text{O}) + \text{H}_2^{16}\text{O}$.⁴⁶

Furthermore, both m/z 289/291 (P1) and 323/325 (P2) shift by +2 Da in D_2O :AN mixtures, as expected from the presence of two exchangeable H(D) atoms (Figure 2A). The key finding regarding the mechanism of formation of P1 is that the m/z 289/291 signals shift by +4 Da in H_2^{18}O :AN mixtures. This means that the O atoms of P1 are derived from the participation of two water molecules rather than from O_3 . In other words, the formation of P1 involves α -HH and water. From the above, given that P1 has two exchangeable H atoms (Figure 2A) and increases as α -HH decreases with similar rate constants (within experimental error; see below) (Figure 1), we assign P1 to a functionalized gem-diol [4-((1R,4S)-4-(5,5-dihydroxypent-1-en-2-yl)-2,2-dimethylcyclobutyl)butan-2-one] produced from the substitution of OH for OOH in α -HH, which generates H_2O_2 as a coproduct (Scheme 2). We discard the possibility that P1 were a noncovalent hydrate of the aldehyde group because, by lacking two (geminal in this case) $-\text{OH}$ groups, it would not bind Cl^- and therefore be undetectable by mass spectrometry.

In revealing contrast, the m/z 323/325 signals shift by only +2 Da in H_2^{18}O :AN mixtures, as expected from a species derived from the ozonolysis of both the exo and endo C=C

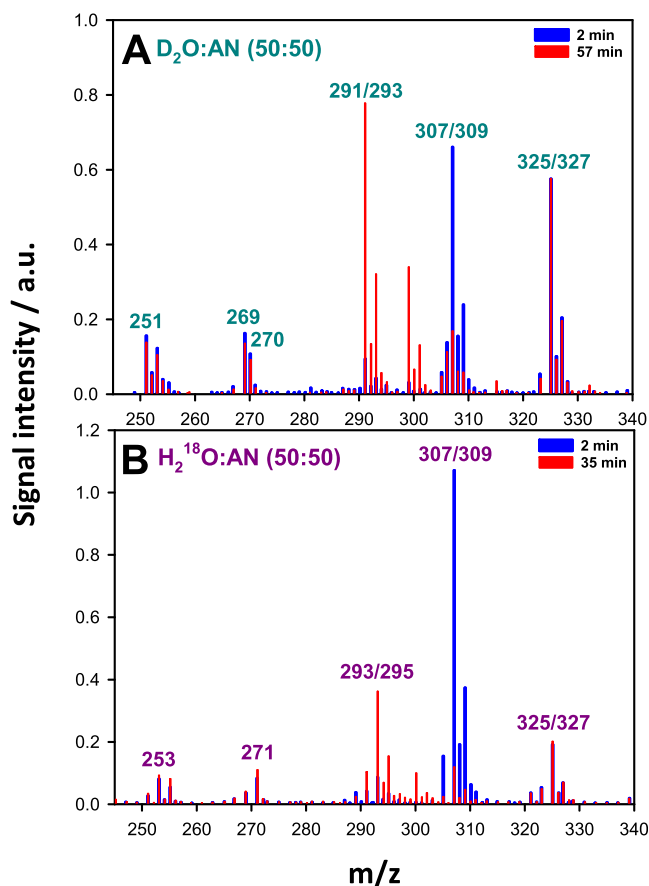


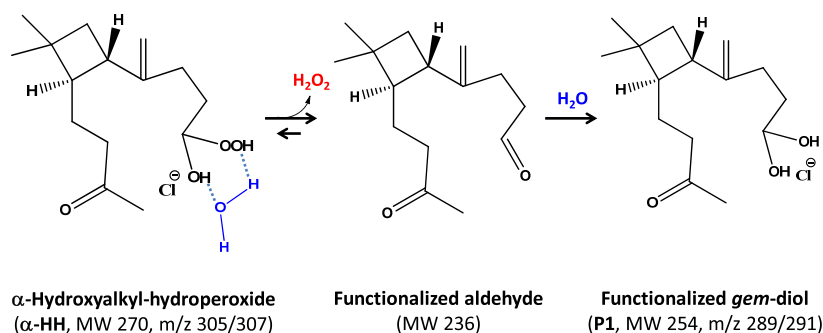
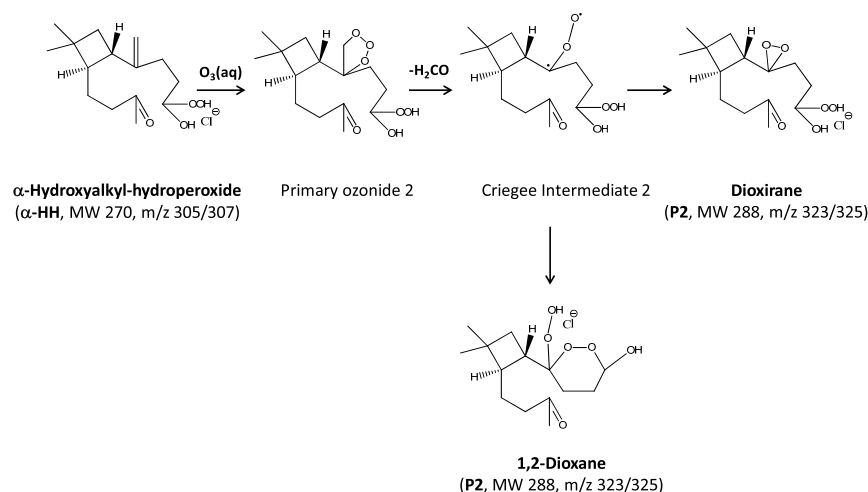
Figure 2. Negative ion mass spectra of (1 mM β -caryophyllene + 0.2 mM NaCl + $[\text{O}_3]_0 = 0.04 \text{ mM}$) solutions in (A) D_2O :AN and (B) H_2^{18}O :AN, both 50% by vol.

bonds of β -C rather than from the participation of a second H_2O molecule in its formation (Scheme 3).

Kinetic Measurements. Figure 3 shows the temporal profiles of the above-mentioned signals in 50% water by volume W:AN solvent mixtures ($[\text{H}_2\text{O}] = 27.8 \text{ M}$).

The decay of m/z 305/307 signal intensities could be fitted with single-exponential decay functions, $S = S_0 \exp(-k_{\text{decay}}t)$, which yielded rate constants for step 1: $k_{\text{decay}} = k_1$. Five independent measurements in W:AN (50:50) solutions led to $k_1 = (3.2 \pm 0.7) \times 10^{-4} \text{ s}^{-1}$. We verified that the decay of α -HH is not affected over $7 \leq [\beta\text{-C}]_0/[\text{O}_3]_0 \leq 34$ variations of the reactants ratio, thereby excluding the participation of β -C in α -HH decay. The rise of P1 (m/z 289/291) signals in W:AN (50:50) was fitted with a single-exponential growth to a maximum function, $S = S_{\infty}[1 - \exp(-k_{\text{P1,rise}}t)]$, which led to $k_{\text{P1,rise}} = (2.7 \pm 0.6) \times 10^{-4} \text{ s}^{-1}$ (from five independent experiments). It is apparent that the rate constants of m/z 305/307 signal decay, k_1 , and m/z 289/291 (P1) growth, $k_{\text{P1,rise}}$, are identical within experimental error, as expected from P1 being a direct product of α -HH decomposition (Scheme 2). This finding implies that the hydration of the functionalized aldehyde is much faster than its formation (Scheme 2), the latter being the rate-determining step.

Figures S4–S7 show the temporal profiles of all signals in 10, 20, 30, and 40% W:AN solvent mixtures. These mixtures span the $[\text{H}_2\text{O}] = 5.6\text{--}22.2 \text{ M}$ range. α -HH signals decay as $S = S_0 \exp(-k_1t)$, while other signals (apart from the m/z 251 signals; see above) increase with time as $S = S_0 + S_{\infty}[1 -$

Scheme 2. Mechanism of Reaction between α -HH and WaterScheme 3. Mechanism of Formation of the m/z 323/325 Products^a

^aWe show the most likely, among many, structural and stereo isomers (see text).

$\exp(-kt)$], except in the case of the 10% water mixture (see below). Note that α -HH signals decay to zero in all cases, except for 10% water, thereby implying that the equilibrium α -HH = P1 + H_2O_2 is completely shifted to the right side (Scheme 2). Using the reported equilibrium constant between hydroxymethyl-hydroperoxide ($\text{H}_2\text{C}(\text{OH})\text{OOH}$) and H_2CO + H_2O_2 in aqueous solution, $K_{\text{eq}} = [\text{H}_2\text{C}(\text{OH})\text{OOH}]/[\text{H}_2\text{CO}][\text{H}_2\text{O}_2] = 160 \text{ M}^{-1}$ at 298 K as a reference,⁴⁷ we estimate that >89% of 1 mM $\text{H}_2\text{C}(\text{OH})\text{OOH}$ would be converted to products. This may be also the case of α -HH. We derived first-order rate constants $k_1 = (1.4 \pm 0.6) \times 10^{-4}$, $(1.4 \pm 0.2) \times 10^{-4}$, and $(1.7 \pm 0.4) \times 10^{-4} \text{ s}^{-1}$ in 20, 30, and 40 vol % W, respectively, at $298 \pm 3 \text{ K}$. These k_1 values are plotted as functions of water volume % in Figure 4. We also derived k_1 from experiments in the presence of excess (100 mM) THF (an OH radical scavenger): $k_{1,\text{THF}} = (5.4 \pm 6.1) \times 10^{-5}$, $(1.3 \pm 0.1) \times 10^{-4}$, $(1.8 \pm 0.5) \times 10^{-4}$, $(2.4 \pm 0.7) \times 10^{-4} \text{ s}^{-1}$ in 20, 30, 40, and 50 vol % W, respectively (Figure S8). It is apparent that THF has a minor if any effect on the kinetics.

Figure 4 shows that the persistence (e -folding time) of α -HH, $\tau_{1/e} = 1/k_1$, increases in a nonlinear manner as the water content of the solvent mixtures decreases. Thus, e -folding times increase from $\tau_{1/e} = (52 \pm 10) \text{ min}$ in 50% water to $\tau_{1/e} = (119 \pm 44) \text{ min}$ in 20% water mixtures. Strikingly, this gradual trend does not extend to the 10% water mixture, where α -HH persists much longer and decays following a double- rather than a single-exponential function, $S = S_0 \exp(-k_1 t) + S_0' \exp(-k_1' t)$ (see Figure S4). Thus, under relatively dry

conditions (i.e., $\leq 10\%$ water content), only $\sim 23\%$ of the initial α -HH is lost at 200 min and not more than 45% after 1912 min = 32 h (Figure S9). We note that our k_1 values in >10% water mixtures are within an order of magnitude of those reported for the decay of α -acyloxyalkyl-hydroperoxides (α -AAHPs) in aqueous mixtures,³⁹ suggesting a similar decomposition mechanism. The same report indicated the enhanced stability of α -AAHPs in nonaqueous solvents such as methanol and acetonitrile,³⁹ in line with our observations.

It should be realized that if these macroscopically homogeneous, visually clear mixtures (water and acetonitrile are miscible in all proportions) were also homogeneous at the molecular scale, water would always be available in large excess to all solutes in this system. If that were the case, the addition of water to the CI^{3,48} and the reaction of water with α -HH, reaction R1, would be independent of water content. Any dependence on water content, particularly a nonlinear one such as that of Figure 4, therefore reveals that CI and α -HH are confined in discrete domains with limited accessibility to water. This phenomenon is consistent with experiments showing that the components of visually homogeneous solvent mixtures are not randomly mixed at the molecular scale.^{49–51} Small-angle neutron and dynamic light scattering experiments detect short-lived (<50 ps), short-ranged ($\sim 1 \text{ nm}$) concentration fluctuations in most water–hydrotrope mixtures such as the W:AN system.^{50–52} In the presence of hydrophobic solutes, such as β -C in our experiments, such fluctuations are stabilized and extend into persistent, mesoscopic (10–100

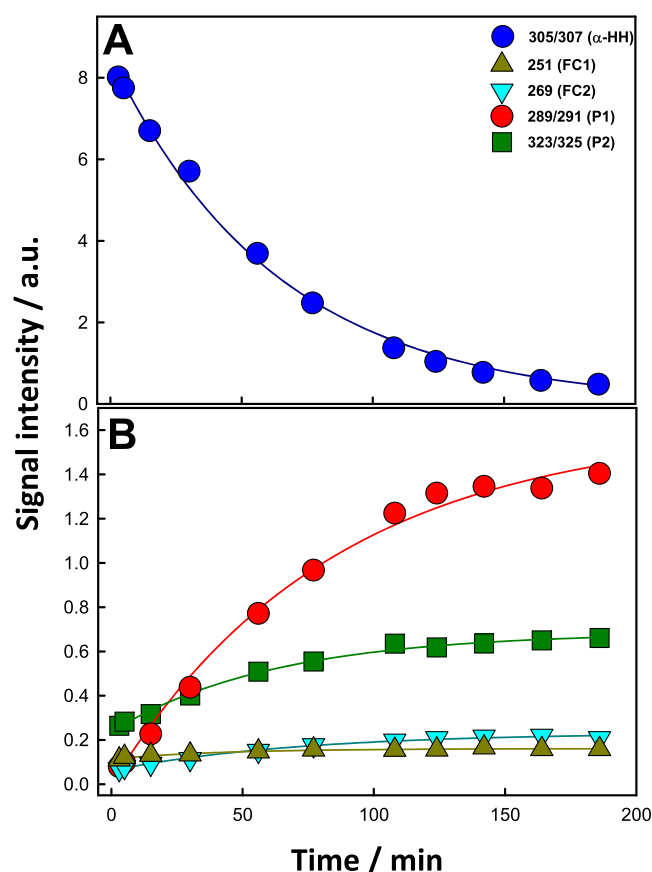


Figure 3. Temporal profiles of α -HH (m/z 305/307) (A) and products (m/z 251, 269, 289/291, 323/325) (B) from (1 mM β -caryophyllene + 0.2 mM NaCl + $[\text{O}_3]_0 = 0.04$ mM) in W:AN (50:50 = vol:vol, $[\text{W}] = 27.8$ M) mixtures as a function of time. Lines for m/z 305/307 and 289/291 correspond to single-exponential decay and single-exponential rise to a maximum regression, $S = S_0 \exp(-k_1 t)$ and $S_\infty [1 - \exp(-k_1 t)]$, respectively. Other product signals are fitted with $S = S_0 + S_\infty [1 - \exp(-kt)]$. See the text for details.

nm) inhomogeneities.^{53–55} The message is that the existence of nanometer-level inhomogeneities in all “internally mixed” solutions is a general phenomenon that could play hitherto unrecognized roles in atmospheric aqueous media.

We have recently shown that the formation of α -HH in the interfacial ozonolysis of β -C in W:AN, W:THF, and W:1,4-dioxane mixtures are roughly exponential rather than linear functions of water content.⁴⁸ The overall exponential dependences on water content, moreover, are not smooth but display significant structure.⁴⁸ We ascribed these phenomena to the fact that the hydrophobe β -C preferentially resides and the CI is generated by ozonolysis in W_nAN_m clusters rich in acetonitrile. Water accessibility to the CI is therefore controlled by the composition and internal dynamics of the W_nAN_m clusters. A similar consideration applies to the amphiphilic α -HH. From this perspective, the stability jump experienced by α -HH in going from 20:80 to 10:90 W:AN mixtures, where $\sim 55\%$ α -HH is recovered after 32 h, means that α -HH is not randomly produced in molecularly homogeneous W:AN mixtures but in discrete W_nAN_m clusters whose composition is a nonlinear function of water content. The sigmoidal dependence of k_1 on water content (Figure 4) reveals that the reaction R1 rates are determined by the composition of microheterogeneous W_nAN_m clusters rather

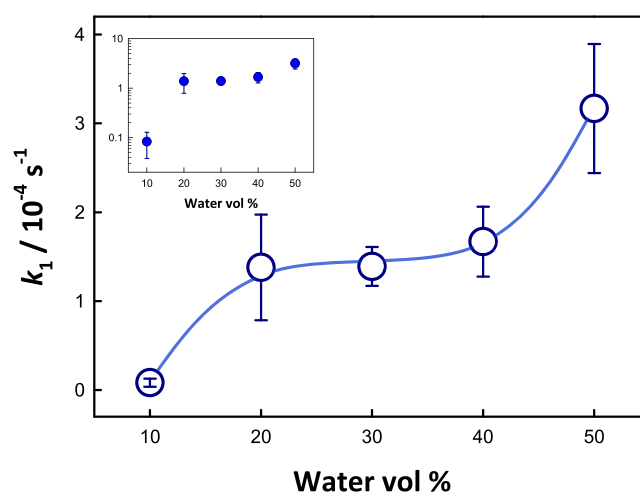


Figure 4. First-order rate constant, k_1 , for α -HH decay (m/z 305/307) in 1 mM β -caryophyllene + 0.2 mM NaCl + $[\text{O}_3]_0 \approx 0.04$ mM at 298 ± 3 K as a function of water vol % in W:AN mixtures. k_1 values are derived by fitting α -HH decays with single exponentials, $S = S_0 \exp(-k_1 t)$, except in the case of 10 vol % W mixtures where α -HH decay was fitted with a double exponential, $S = S_0 \exp(-k_0 t) + S'_0 \exp(-k_1 t)$. See the text for details. Error bars are derived from 3–5 replicate experiments. The line is a visual guide. The inset shows the semilog plot.

than by the average composition of the visually homogeneous “internally mixed” W:AN mixtures. Self-clustering of hydrophobe molecules into discrete domains in macroscopically homogeneous “internally mixed” solvent mixtures may significantly affect chemistry in such media. Because this is a general phenomenon, nonlinear dependences of reaction rates on the composition of aqueous organic media should be expected to be the norm rather than exceptions.

The finding that the thermal stability of α -HH strongly depends on the water content of the aerosol has significant implications regarding the fate of the typically amphiphilic α -HHs in general, their role in aerosol chemistry, and in the analytical protocols. The rapid decay (roughly within a couple of hours) observed under most conditions (water content $> 10\%$ by volume) implies that α -HHs can be lost promptly, thereby introducing a hitherto unrecognized parameter in the analytical procedures employed in their detection and quantification. Such losses may partially account for inconsistent reports on the amounts of hydroperoxides detected by offline chemical analysis of aerosols collected in the field or synthesized in the laboratory.⁵⁶

The relatively short lifetimes of α -HHs exclude their solar photolysis as a significant decay mechanism. Atmospheric photolysis of α -HHs species containing both $-\text{OOH}$ and $\text{C}=\text{O}$ groups is expected to proceed via excitation of the carbonyl chromophore and will take several hours.^{20,57} Alternatively, the decay of ROOH could be accelerated by iron and copper ions via Fenton-type chemistry, possibly involving RO and OH radicals.⁵⁸ By using representative values of $[\text{Fe}^{2+}] \approx 10^{-7}$ M, $[\alpha\text{-HH}] \approx 10^{-6}$ M in aqueous aerosol/cloud droplets,^{47,59,60} and $k(\text{Fe}^{2+} + \alpha\text{-HH}) \approx 20 \text{ M}^{-1} \text{ s}^{-1}$,⁶⁰ we derive a value for the half-life of α -HH in the presence of Fe^{2+} of ~ 14 h, i.e., much longer than the $\tau_{1/e} < 2$ h at $\geq 20\%$ water content determined in the present study for the decomposition of α -HH via the mechanism of Scheme 2. Therefore, our study suggests that the persistence of α -HH in ambient atmospheric particles is largely

controlled by water content rather than by photolysis or Fenton-type chemistry. Finally, it is important to realize that the decomposition of α -HHs, by producing H_2O_2 as the coproduct of P1, preserves the peroxide content of the aerosol and hence the potential adverse health effects of particulate matter pollutants.^{61,62}

EXPERIMENTAL SECTION

The experimental method for bulk ozonolysis has been described elsewhere⁶³ and is only briefly mentioned here. Figure S1 shows a schematic diagram of our experimental procedure for preparing α -HHs in solvent mixtures. β -C was dissolved in W:AN mixtures (10 mL) containing 0.4 mM NaCl in a 25 mL vial. An O_3 solution was separately prepared by flowing ultrahigh purity $\text{O}_2(\text{g})$ (>99.999%) through a commercial ozonizer (KSQ-050, Kotohira, Japan) and then into W:AN mixtures of the same composition (10 mL) contained in another vial. The $\text{O}_3(\text{g})/\text{O}_2(\text{g})$ mixtures issuing the ozonizer were carried to and sparged into the vial through Teflon tubing (3 mm diameter) at a 1 L/min flow rate (regulated by a digital mass flow controller) for ≤ 20 s. The initial concentration of O_3 , $[\text{O}_3]_0$, was determined (before mixing with the β -C solution) with a UV-vis spectrometer (Agilent 8453) using the molar extinction coefficient of O_3 at 258 nm: $\epsilon_{258\text{ nm}} = 3840\text{ M}^{-1}\text{ cm}^{-1}$.⁶⁴ To minimize unwanted secondary reactions, $[\beta\text{-C}]_0$ was always kept larger than $[\text{O}_3]_0$, i.e., $[\beta\text{-C}]_0/[\text{O}_3]_0 > 7$. Volumes of 2.5 mL of each of the two solutions were mixed in a glass syringe (5 mL) (covered with aluminum foil to avoid unwanted photolysis) and immediately injected (by a syringe pump, at $100\text{ }\mu\text{L min}^{-1}$, Harvard apparatus) into an electrospray ionization mass spectrometer (Agilent 6130 Quadrupole LC/MS electrospray system at NIES, Japan). The α -HHs generated by this procedure, as well as its decomposition products, were monitored as functions of time (recorded by a digital stopwatch triggered at the mixing of two solutions).

The key feature of the present method is the capability to detect neutral α -HHs by adding inert NaCl⁶⁵ to reaction mixtures.³ We have found that α -HHs, similar to other species having multifunctional groups, such as $-\text{OOH}$, $-\text{OH}$, and $-\text{C}=\text{O}$, can be detected as chloride adducts ($m/z = M + 35/37$) by mass spectrometry.^{3,5–7,36,46} We emphasize that chloride is inert toward O_3 ($k \approx 1 \times 10^{-2}\text{ M}^{-1}\text{ s}^{-1}$) under present conditions.^{3,65}

Experimental conditions for the operation of the mass spectrometer were as follows: drying nitrogen gas flow rate: 12 L min^{-1} ; drying nitrogen gas temperature: $340\text{ }^\circ\text{C}$; solution inlet injector voltage: $+3.5\text{ kV}$ relative to ground; fragmentor voltage: 60 V . All solutions were prepared in ultrapure water (resistivity $\geq 18.2\text{ M}\Omega\text{ cm}$ at 298 K) from a Millipore Milli-Q water purification system and used within a day. Chemicals β -caryophyllene (>90%, Tokyo Chemical Industry), acetonitrile ($\geq 99.8\%$, Wako), tetrahydrofuran ($\geq 99.8\%$, stabilizer-free, Wako), D_2O (>99.9 atom % D, Sigma-Aldrich), H_2^{18}O ($\geq 97\%$, Santa Cruz Biotechnologies), and NaCl ($\geq 99.999\%$, Sigma-Aldrich) were used as received.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.9b01953.

Schematic setup and procedure, additional negative ion mass spectra of the species studies, temporal profile of pH values, semilog plots of mass spectral signal intensities vs time in various water vol %, and plot of first-order rate constants derived in the presence of 100 mM THF vs water vol % (PDF)

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Author Contributions

S.E. designed the research; J.Q. and S.E. performed experiments; and S.E. contributed new reagents/analytic tools. All authors analyzed data and wrote the paper.

Notes

The authors declare no competing financial interest.

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